Oil Recovery Method Using Alkali And Alkylaryl Sulfonate Surfactants Derived From Broad Distribution Alpha-Olefins

FIELD OF INVENTION

The present invention is directed to enhanced oil recovery (EOR). More specifically, the present invention is directed to enhanced oil recovery of crude oil using a mixture of alkali(s) and alkylaryl sulfonate surfactant derived from broad distribution alpha-olefins.

BACKGROUND OF THE INVENTION

This invention is an improvement over US Patent 6,269,881 and much of the background material is drawn from this reference and all references included in US Patent 6,269,881 are included herein.

Alkylaryl sulfonates with narrow distribution carbon chains have long been recognized as promising surfactants for EOR. They can be manufactured in fairly large quantities and can generate adequate phase behavior and low interfacial tensions (IFT) with oils under favorable conditions. However, pure alkylaryl sulfonates such as hexadecyl benzene sulfonate or those having a narrow distribution carbon chains, cannot generate adequate phase behavior and low interfacial tension with a wide range of crude oils especially when dealing with heavier crude oils, particularly those with a high wax content. They must be used at relatively high concentrations and they do not form normal phase behavior when mixed with crude oil and brine of varying salinity. Furthermore, when used together with alkali in alkali surfactant flood, alkylaryl sulfonates with narrow distribution carbon chains are only effective over limited ranges of alkali which is detrimental to efficient oil recovery. Pure alkylaryl sulfonates or those with narrow distribution carbon chains have other disadvantages. With low oil prices, the

surfactant used to recover such oil must be cost effective. Prior methods, which use alkylaryl sulfonates with narrow distribution of carbon chain lengths, increase the cost because of the large quantities of unsuitable byproducts and/or the need for more tightly controlled reaction conditions or specialized catalysts required to manufacture such surfactants.

Alkyl aryl surfactants derived from broad distribution alpha-olefins have recently been recognized as promising for enhanced oil recovery by surfactant floods as noted in US Patent 6,269,881. However, use of the broad distribution alpha-olefins surfactants generally requires 0.5% to 3.0% and most preferably 1.0 to 1.5% as noted in US Patent 6,269,881. The higher concentration of the surfactant and the optima salinity required are uneconomical and unsatisfactory for a large quantity surfactant flood. Also, Malmberg and Smith in "Improved Oil Recovery by Surfactant and Polymer Flooding" Shah and Schechter ed., (Academic press 1977), pp. 282 found that adsorption increases with increasing average equivalent weight of sulfonates so that the higher molecular weight fractions of these broad distribution surfactants are subject to selective adsorption.

Thus it would be highly desirable to have a recovery method and composition useful for recovering crude oil that employs ingredients that are readily available in large quantities at reasonable cost. Also it would be desirable to have a composition that includes a broad spectrum of carbon chain lengths so substantially complete production runs can be used. Also it would be desirable if such compositions could be rendered

effective at low surfactant concentrations and not be subject to chromatographic separation due to selective adsorption while propagating through the oil containing reservoir formation because of the increasing average equivalent weight of sulfonates. Also it would be desirable to have a composition that is not dependent on an optimum salinity for optimum performance. Also it would be desirable to have a composition that is effective over wide ranges of alkali.

SUMMARY OF THE INVENTION

This invention provides an improvement over the closest existing art described in US Patent 6,269,881 and also provides other benefits that are not obvious to the ordinary skilled artisan which arise from the inclusion of alkali(s) with the surfactant derived from broad distribution alpha-olefins in the method of recovering oil from subterranean hydrocarbon containing formations and in the composition of enhanced oil recovery to displace said composition through the subterranean formation. The method is especially useful when the reservoir oil has higher wax content. The present invention includes a method of recovering crude oil from a subterranean hydrocarbon containing formation which comprises (a) injecting into said formation through an injection well an aqueous solution containing an effective amount of one or more alkali(s) along with an effective amount of alkylaryl sulfonate surfactant made by alkylating and sulfonating aromatic compounds and an alpha-olefin stream having a broad distribution in olefin carbon numbers, the olefin stream is the carbon chain C_{10} bottoms of a commercial ethylene synthesis alpha-olefin reactor and comprises C_{10+} through C_{30+} carbon chain fractions, and wherein the aromatic compound is selected from the group consisting of

benzene, toluene, xylene, ethyl benzene, or mixtures thereof, and then neutralizing the resulting alkylaryl sulfonic acid, and (b) displacing said solution into the formation to recover hydrocarbons from a production well.

The present invention also includes an alkali(s) and alkylaryl sulfonate surfactant composition for enhanced oil recovery giving the improvements of requiring ultra-low surfactant concentration and providing ultra-low interfacial tensions over a wide range of alkali(s) concentrations. Said composition comprises one or more alkali(s) along with an alkylaryl sulfonate wherein the alkyl chain includes C_{12} to C_{30+} carbon chain lengths and wherein the carbon chain is straight, branched or mixtures thereof, and wherein the aryl group is selected from the group benzene, toluene, xylene, ethyl benzene, or mixtures thereof. The alkali(s) that may be used include any inorganic or organic salt, or the mixture thereof, that is capable of increasing the pH of the injection solution above 9.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the interfacial tension values obtained with various concentrations of NaOH and the three examples of alklaryl sulfonates described in this patent.

Figure 1 shows the interfacial tension values obtained with various concentrations of one of the examples from this patent, OXS-1228, when no NaOH is added.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is the inclusion of alkali(s) along with alkylaryl sulfonates derived from a broad distribution of alpha-olefins greater than C10 to C58 or more, or preferably the entire C10 bottoms fraction, i.e., greater than C10 of an alpha-olefin process. Suitable ranges are C12 to C40 preferably ranges such as C10 to C32; C12 to C28; and C10 to C24. In contrast, conventionally used alkylaryl sulfonates generally focus on a narrow range of olefin carbon numbers, such as C12 xylene sulfonate, C12 benzene sulfonate, C16 xylene sulfonate, C18 toluene sulfonate, and C20-24 toluene sulfonate. In these cases, other carbon chain lengths made during the reaction must be separated out. This adds to the cost of the specifically used product. In commercial applications of alkali surfactant floods, the quantity of surfactant required is huge, often exceeding 100 million pounds lbs. If only a narrow fraction of the alpha-olefins are used to make the surfactant, the required olefin plant capacity would exceed a few billion pounds, which is not presently available. While one can build a new plant to meet the demand of the surfactant flood, the unused olefin fractions cannot be readily used for other purposes and, therefore, must be accounted for in the cost of the olefin feedstocks for the surfactant. Thus the present invention of the EOR composition and process of recovering oil using surfactant derived from broad distribution alpha-olefins along with alkali(s) permits better use of the whole spectrum of an alpha-olefin plant's products. Since the current alpha-olefin market is largely driven by the demand in C10 and lower fractions use in plastic production such as polyethylene and/or polypropylene, the use of C10 bottoms (i.e., C12 and higher fractions) in the present invention does not pose a conflict or tradeoff. It actually provides for a more synergistic use of the plants total output. In fact, taking the entire C10 bottoms, i.e., C12 and higher, would eliminate

many costly fractionation steps, thus further lowering the cost of the alpha-olefin feedstock for the surfactant.

The surfactant derived from broad distribution alpha-olefins is used in an aqueous injection solution in combination with alkali(s), and optionally a conventional cosurfactant/solvent and a polymer to increase the recovery of crude oil from a subterranean formation. The most preferred broad distribution alkylaryl sulfonate is the sodium salt of xylene sulfonic acid. Alkalis that may be used include any inorganic or organic compounds or mixtures of two or more that is capable of increasing the pH of the injection solution above pH 9. These include, but are not limited to, sodium, potassium, or ammonium hydroxide; sodium, potassium, or ammonium carbonate; sodium, potassium, or ammonium silicate, as well as any other compounds that give a pH in excess of 9 in the injection solution. The most preferred alkali is sodium hydroxide or sodium carbonate.

Broad distribution alkyl aryl sulfonate EOR surfactant can be prepared by the process described in US Patent 6,269,881 wherein the alkylaryl sulfonate preparation involves three steps: three steps: alkylation, sulfonation and neutralization.

Similar broad distribution alkylaryl sulfonates can be prepared by the process described in US Patent 6,043,391 where the broad distribution alpha-olefin is first sulfonated in a thin film reactor with SO3/Air to form the olefin sulfonic acid. This olefin sulfonic acid is then reacted with a suitable aromatic compound such as benzene, toluene, xylene, or

mixtures thereof, to form the arylalkyl sulfonic acid that is then neutralized with a strong base such as sodium hydroxide to form the sulfonate. It should be noted that the synthesis procedure described in US Patent 6,043,391 is the reverse of the procedure described in US Patent 6,269,881. In US Patent 6,269,881, the aromatic compound is first alkylated with the broad distribution alpha-olefins and then the resulting alkylate is sulfonated to form an alkylaryl sulfonic acid. In the US Patent 6,043,391 procedure the broad distribution alpha-olefins are first sulfonated and the resulting alpha-olefin sulfonic acid is used to alkylate the aromatic compound. One advantage of the process described in US Patent 6,043,391 is that the need for a separate alkylation plant is eliminated. This results in considerable up-front savings as well as elimination of on-going operational cost associated with an alkylation plant.

The use of xylene as the aromatic compound for alkylation is especially preferred because of its higher boiling point that allows it to be handled without pressure during alkylation and/or sulfoalkylation. While not described here, one can certainly use a mixture of benzene, ethylbenzene, toluene, and xylene of various fractions or any of these aromatic compounds individually to optimize the surfactant for a specific reservoir application or to take advantage of the aromatics market conditions.

The present invention, a composition comprising a mixture of alkali(s) and a alkylaryl sulfonate surfactant derived from a broad distribution of alpha-olefins, is injected into an injection well in an effective amount to allow the recovery of oil from a production well by lowering the IFT between trapped oil and the injection solution. The injection well and

the producing well may be the same or different wells or a combination of both. The concentration ranges of the present invention using the neutralized form of the surfactant derived from the broad distribution of alpha-olefins are from 0.025% to 0.5% by weight, preferably 0.05% to 0.2% by weight, and most preferably 0.05% to 0.1% by weight. The concentration ranges of alkali(s) are 0.1 to 3.0% by weight, preferably 0.5 to 2.0% by weight and most preferably 0.5 to 1.0% by weight. A cosurfactant/solvent may be included at approximately the same concentration as the surfactant and is usually formulated with the surfactant in a concentrated form that is diluted with injection water to the appropriate final concentration at the injection site. An alcohol or ether such as Iso-propanol, sec-butanol or ethylene glycol monobutyl ether (EB) can be used as the cosurfactant/solvent.

Polymers, such as those commonly employed for such purposes, may be included to control the mobility of the injection solution. Such polymers include, but are not limited to, xanthan gum, partially hydrolyzed polyacrylamides and copolymers of 2-acrylamido-2-methylpropane sulfonic acid and polyacrylamide commonly referred to as AMPS copolymer. Polymers are used in the range of about 500 to about 2000 PPM in order to match or exceed the reservoir oil viscosity under reservoir conditions of temperature and pressure.

The present invention includes the addition of a composition comprising a mixture of alkali(s) and an alkylaryl sulfonate surfactant derived from a broad distribution of alpha-olefins into an oil-bearing subterranean formation at concentration levels of surfactant

between 0.025% and 0.5% as opposed to US Patent 6,269,881 that requires 0.5% to 3.0%, thus providing a significant cost advantage. The alkali(s) also acts synergistically with the surfactant to give optimum performance as demonstrated by ultra-low interfacial tensions obtained at very low surfactant concentrations. The ultra-low IFTs are not obtainable without the use of such alkali(s) at such low surfactant concentrations. In addition, the alkali reduces the chromatographic separation of the sulfonate surfactant containing a broad distribution of alkyl chain lengths by increasing the pH of the injection water. Increasing the pH to exceed the iso-electric point of the reservoir rock decreases the electrical attraction that might normally occur between the positively charged surface and the negatively charge anionic surfactant. See for example, Baviere, "Basic Concepts on Enhanced Oil Recovery Processes" (Elsevier 1991) pp. 147-149. The present invention also does not require any adjustment of the injection brine to the optimum salinity. Adjusting the injection brine to the optimum salinity will give ultra-low IFT without the use of alkali, however; as is commonly known to those familiar with the art, the salinity cannot be maintained at the optimum level and will deviate from the optimum as the solution progresses through the oil-bearing reservoir. This is due to adsorption of electrolyte and mixing with connate brine. Therefore a system not dependent on optimum salinity would be desirable.

The use of alkali(s) with surfactant has been previous described in the literature; however, the alkali surfactant processes described in the prior art using narrow distribution alkylaryl sulfonates work only over a narrow range of alkali where ultra-low interfacial tensions are obtained. Even when an optimum ratio of surfactant to alkali is

introduced into the reservoir, the ratio of the two will change as they propagate through the reservoir. This is due to the preferential adsorption of the alkali onto the formation causing the ratio of alkali to surfactant to deviate from the optimum. Therefore, being able to obtain ultra-low IFT over a wide range of alkali is very important for oil recovery optimization. The present invention includes alkali(s) with a surfactant derived from a broad distribution of alpha-olefins. Unexpectedly, we have found the use of alkali(s) with surfactant derived from broad distribution alpha-olefins gives additional advantages heretofore not described in the art. Using alkali(s) combined with an alkylaryl surfactant derived from broad distribution alpha-olefins widens the range of alkali that can be used to give ultra-low IFT suitable for oil recovery. This wide range of alkali where ultra-low IFT is observed is not obtainable with the surfactant made from narrow distribution carbon ranges.

In a process similar to that described in US Patent 6,269,881, the C12 to C28 cut of an alpha-olefin was reacted with mixed xylene, consisting of 90% o-xylene and the other 10% a mixture of meta-xylene and para-xylene to form alkylates using $AlCl_3$ catalyst, and subsequently sulfonated with SO_3. This surfactant is designated as OXS12-28.

In another example, using the process similar to that described in US Patent 6,269,881, the C16 cut of an alpha-olefin was reacted with a mixed xylene, consisting of 90% o-xylene and the other 10% a mixture of meta-xylene and para-xylene to form alkylates using $AlCl_3$ catalyst, which are subsequently sulfonated with SO_3. This surfactant is designated as OXS16.

In another example, using the process described in US Patent 6,043,391, the C12 to C28 cut of an alpha-olefin is sulfonated with SO_3 to form alpha-olefin sulfonic acids that are subsequently reacted with a mixed xylene, consisting of 90% o-xylene and the other 10% a mixture of meta-xylene and para-xylene. This surfactant is designated OXS12-28-N.

The following examples compare the results using the previously described OXS12-28, OXS16 and OSX 12-28-N. A surfactant concentrate of each example was prepared by neutralizing the sulfonic acid in a mixture of water and EB. The concentrate contained 50% by weight sodium salt of the sulfonic acid, 25% by weight EB and the remainder water. A simulated injection brine was used containing 4500 ppm of total dissolved solids with 310 ppm of di-valent cations. The crude oil used had a density of 0.834 gm/cc (38.2 API Gravity) @ 25 °C.

Interfacial tensions (IFT) were measured at 45°C using a University of Texas Model 500 spinning drop interfacial tensiometer. Figure 1 shows the IFT of the simulated injection brines each containing 0.2% by weight of each of the surfactant concentrates and various concentrations of NaOH against the crude oil at 45°C. The IFT of the three samples are in the range of about 1.0 mN/m without the addition of NaOH. This is not sufficient for removing oil as is commonly known to those familiar with the art as practiced in this field, and as described by Austad and Miller in “Surfactants-Fundamentals and Applications in the Petroleum Industry”, pp. 205-207. Here the

authors discuss the concept of capillary number and have determined that the interfacial tension must be lowered to a value of between 0.01 to 0.001 mN/m to mobilize trapped discontinuous oil in a reservoir. The concentration ranges of the alkali that provides adequate IFT with the surfactant is important. A wider range means that the IFT lowering properties of the surfactant are less sensitive to the alkali concentrations which is very important to the oil recovery. Figure 1 also shows that the optimum IFT range where the IFT is 10^{-3} mN/m for OXS 16 is approximately 0.8% to 1.1% NaOH. The optimum IFT range for OXS 12-28 and OXS 12-28-N are from approximately 0.5% to 1.6% NaOH. The data indicates that OSX 12-28 and OSX 12-28-N, that are the surfactants derived from broad distribution alpha-olefins provided tremendous improvement over OSX 16, which is the surfactant made from the narrow distribution of alpha-olefin.

Figure 2 shows the IFT results obtained using various concentrations of OXS 12-28 without NaOH. The data shows that the OXS 12-28 alone is not very effective at the low concentrations ranges of 0.1 – 0.5%. In order to use this surfactant at cost-effective concentrations, an alkali is necessary. This is evident when comparing the IFT values obtained for OXS 12-28 in Figures 1 and 2.

The above examples served to illustrate the advantages and unexpected benefits obtained using the method and composition of the present invention. Specifically the inclusion of alkali(s) along with alkylaryl sulfonates derived from broad distribution alpha-olefins provides a composition and a process that uses ultra-low surfactant

concentrations and unexpectedly provides ultra-low IFT over a wide range of alkali concentrations. The present invention improves the performance, efficiency and economics over the traditional alkali surfactant flooding method using narrow distribution of the alkylaryl sulfonates and the surfactant flooding method as disclosed in US patent 6,269,881.

The invention was described with respect to particularly preferred embodiments. Modifications within the scope of the ordinary skilled artisan, e.g., the use of branched alkyl chains and mixture of aryls and particularly o-xylene alkylate(s) combined with alkali(s), are within the scope of the invention and the appended claims.